

COMPOSITION

## FIELD OF THE INVENTION

- 5 The present invention relates to fuel additives. In particular the present invention relates to use of film-forming additives to inhibit and/or prevent cavitation damage on pumping in blends of fuel alcohol with diesel fuel.

## BACKGROUND AND PRIOR ART

10

- Internal combustion engines which function through the medium of compression ignition, conventionally known as diesel engines, are well known to those skilled in the art to generate a significant level of particulate matter during the combustion process. Diesel particulates are formed through the combustion or pyrolysis of hydrocarbon fuels typically known as middle distillates, and typically boiling in the temperature range 180°C to 360°C. Particulates in the exhaust of a diesel engine comprise inorganic ash due to engine wear particles and the combustion products of lubricant oil additives, sulphur containing compounds due to the sulphur in diesel fuel and hydrocarbons from incomplete combustion. These hydrocarbons may be further classified as either soluble material or solid matter, i.e. carbonaceous soot. The soluble hydrocarbon portion of the particulate matter will frequently be described by those skilled in the art as the soluble organic fraction (SOF).

- The particulate matter described above may comprise particles so small as to be invisible to the naked eye. However, diesel engines are also known to emit visible smoke, which represents the obscuration of visible light by clouds of larger particles. These larger particles, also called accumulation particles, may arise from condensation and/or agglomeration of smaller particles, also known as nucleation particles. The visual impact which black exhaust smoke from diesel engine exhausts may have on the beholder is almost universally negative. Black exhaust smoke is perceived as a serious source of air pollution resulting in damage to buildings and other property. In addition, all the above-described particulate emissions are also widely understood to represent a hazard to human health.

- 35 Governments in many countries have enacted legislation to reduce permitted levels of

particulate emissions from diesel engines over recent years. Engine manufacturers have responded to the legislation with the result that in many countries new diesel engines consistently emit lower levels of exhaust particulate matter than older engine designs. However one of the attractive features of the diesel engine for operators and users is its robustness and long life. Diesel engines may be in use for ten, fifteen or twenty years, or, in exceptional cases, even longer. These older engines, while providing very satisfactory service for vehicle owners or operators, nevertheless continue to emit pollutants, in particular particulates and visible smoke, at levels at least as high as when new.

One option which is attractive to governments wishing to improve air quality, is to alter fuel specifications so that all vehicles, as opposed to merely the newer vehicles which are of improved design, produce lower pollution levels. One way in which this can be achieved, is to blend a fuel alcohol such as ethanol into diesel fuel. A blend of ethanol and diesel is commonly known as Ediesel.

The effect of Ediesel on exhaust emissions is subject to some debate and is known to vary between engines of different types. Nevertheless, the most pronounced effect is often found to be in respect of particulate and smoke emissions, which are frequently judged to be the most damaging pollutants emitted by diesel engines. There is thus interest in blends of fuel alcohol and diesel such as Ediesel in many countries of the world, particularly where the diesel vehicle fleet comprises a significant population of older vehicles with unacceptably high particulate emissions.

An additional advantage provided by blends of a fuel alcohol and diesel is the possibility of manufacturing the fuel alcohol, in particular ethanol, initially from renewable products, including waste products of agriculture. This capability provides the opportunity to extend expensive fossil fuel sources, which often need to be imported. Blending fuel alcohol produced from indigenous and renewable sources into diesel fuel can thus make a major and valued contribution to a nation's balance of payments.

The addition of a fuel alcohol to diesel is known to alter the characteristics and physical properties of the base diesel fuel. For example, ethanol boils at a much lower temperature than diesel fuel, whose typical boiling range lies between 180°C and 360°C. When ethanol is added to diesel fuel, the initial boiling point will be reduced very significantly. This is illustrated in Table 1, which contains data obtained with middle

distillates alone and combined with ethanol.

Table 1. Distillation characteristics of middle distillate fuels with and without ethanol.

Distillation characteristics	ULSD3 diesel fuel	ULSD3 + 7.5% vol. ethanol	Kerosene	Kerosene + 7.5% vol ethanol
Initial boiling point °C	175.5	77.0	151.5	77.5
5% recovd. °C	207.5	78.5	163.0	80.0
10% recovd °C	220.5	198.5	165.0	155.5
20% recovd °C	237.5	226.5	169.5	168.0
40% recovd °C	262.5	255.0	179.0	175.0
70% recovd °C	297.5	294.5	197.0	195.5
90% recovd °C	330.5	332.5	216.5	216.0
Final boiling point °C	356.0	354.4	235.5	229.5

5

As is clear from the data in the table, the inclusion of a relatively small volume of ethanol into either a conventional low sulphur diesel fuel, or a kerosene fuel, produces a very significant reduction in the initial boiling point and the 5-10% recovered temperature values (also known as the "front end" by those skilled in the art). Once the ethanol in the front end has boiled off, the rest of the fuel behaves much like a similar base fuel not containing ethanol, as would be expected.

10

In order to produce significant and readily-measured exhaust emissions benefits, significant quantities, such as from about 1-30%, preferably 1-20% by volume of a fuel alcohol, such as ethanol, are required. Where such substantial quantities of a fuel alcohol, such as ethanol, are blended into a fuel the alcohol may contain water and/or the composition may become hygroscopic. Diesel fuels are well-known to encounter water during passage through the supply chain. Whatever the source, the presence of water in the fuel can lead to a phase-separation into aqueous and diesel fuel phases with partition of the alcohol between the two. This is particularly prone to occur at low temperatures and leads to considerable operability problems.

20

To prevent such problems additional additives, such a co-solvent(s) and surfactant(s) are employed. The amounts of each used are, as expected, highly dependant on the particular fuel alcohol, it's water content, anticipated ambient temperatures and, above

25

all, the volume percent alcohol in the fuel. In volume percentage terms, the amounts of each used are typically similar to the volume percent alcohol and are each rarely less than 1%, although quantities as low as 0.5, 0.2 or even 0.1 percent have been claimed, where meaningful (i.e. detectably emissions-reducing) quantities of alcohol are present.

- 5 Where such levels of surfactant are present, industry standard wear tests as hereinafter/before described, indicate that no wear problems should be encountered with that fuel.

The practical consequences of the change in fuel volatility where a fuel alcohol is added to diesel fuel in diesel engine fuel systems can be significant, since such fuel systems are usually designed for the volatility characteristics of conventional middle distillates. Diesel injection pumps, for example, function in such a way that the film of fuel on various internal components may be exposed to reduced pressure at times during each rotational cycle. An example of this phenomenon is the contact between the slotted face washer and the claws on the driver shaft which mate with it, on the Bosch VE rotary diesel injection pump. During normal operation, reduced pressure occurs in the region of the liquid film on the surface of these components. With a conventional diesel fuel or other middle distillate boiling between the ranges indicated in Table 1, the local pressure reduction causes no operational problems. However, with the much more volatile front end of the fuel resulting from blending ethanol into diesel fuel, pressure reduction in the liquid film is thought to produce cavitation.

Cavitation, as is known to those skilled in the art, constitutes the formation and collapse of vapour-filled gas in liquid bubbles associated with fluctuations in local pressure. It is well known that prolonged cavitation can result in surface damage to metallic components. Erosion of apparently hard metallic surfaces is a characteristic feature of prolonged cavitation. Where cavitation occurs in a diesel engine fuel system, for example in the fuel injector pump, eroded particles, collectively called wear debris, circulate within the pump. Such wear debris is frequently abrasive. Circulation of wear debris within the pump accelerates the wear process, while continuing cavitation produces further wear debris, itself abrasive, leading to very accelerated wear in such pumps. Examples of very accelerated wear in Bosch pumps through cavitation, when operating on diesel fuel containing ethanol are in the public domain. Bosch has publicised information on the Internet (address [www.mercosul.bosch.de/50 EPD/epd32](http://www.mercosul.bosch.de/50_EPD/epd32)), which not only details accelerated wear in injector pumps, but also indicates cavitation damage to other fuel

injection equipment components, such as injector needles and pump pressure valve seats. Similar information has also been publicised in Hart's World Fuels Today on 14<sup>th</sup> November 2001.

5 The present invention alleviates the problems of the prior art

#### STATEMENT OF INVENTION

According to a first aspect, the present invention provides a fuel composition comprising  
10 a fuel and a film-forming additive wherein the fuel comprises diesel and a fuel alcohol  
and wherein the film-forming additive is present in the fuel composition in an amount of  
less than 0.1 wt%.

According to a second aspect, the present invention provides use of a film-forming  
15 additive for inhibiting and/or preventing cavitation in a fuel and/or reducing the effects of  
cavitation in a fuel, wherein the fuel comprises diesel and a fuel alcohol.

According to a third aspect, the present invention provides a process for supplying a fuel  
composition to a combustion engine wherein the process comprises (i) pumping the fuel  
20 composition with a rotary pump to supply the fuel composition to the combustion engine  
wherein the fuel composition comprises diesel, a fuel alcohol and a film-forming additive.

It has surprisingly been found that film-forming additives may be used to inhibit and/or  
prevent cavitation in blends of diesel and a fuel alcohol. Addition of a film-forming  
25 additive to a blend of diesel and a fuel alcohol may typically reduce the cavitation-  
induced surface damage of metallic components in a diesel engine fuel system in which  
the fuel blend is used. Additionally, use of a film-forming additive in this manner may  
reduce wear debris generated by cavitation and may also reduce the wear to the diesel  
engine fuel system and in particular the fuel injection equipment which the wear debris  
30 may cause. Thus, use of a film-forming additive according to the present invention, may  
increase the lifetime of the diesel engine fuel system especially fuel injection equipment  
components, such as fuel injector pumps, injector needles and pump pressure seat  
valves.

35 The recent discovery that fuels containing fuel alcohols could cause damage to diesel

engine components was, indeed, surprising. More so was that such fuels could satisfy industry-standard wear tests yet give in-service problems. It has surprisingly been found that film-forming additives may be used to protect engine components from such wear. Without wishing to be bound by theory it is believed that they act to inhibit and/or prevent cavitation in blends comprising diesel and a fuel alcohol

The term "film-forming additive" as used herein, means a substance which, when present in a fuel composition comprising a fuel, the film-forming additive and optional further fuel components, increases the ability of the fuel to form a coating on a metal surface, such as a metal surface within a fuel pump, with which it is contacted.

Particularly useful as a film-forming additive according to the present invention is a substance capable of providing a fuel with which it is contacted with a fuel quality parameter whereby wear between two metal surfaces in contact with each other and with the fuel in a test apparatus is limited to a permitted maximum level. Limitation of wear in a test apparatus may be determined by exceeding a minimum applied load of greater than 2800g, as in the Scuffing Load Ball-On-Cylinder Lubricity Evaluator method (SLBOCLE - ASTM D 6078). Alternatively, limitation of wear in a test apparatus may be determined by not exceeding a wear limit, as in the High Frequency Reciprocation Rig method (HFRR-ASTM D 6079) of 460 micron wear scar diameter (WSD) at 60°C. Limitation of wear may also be measured using the HFRR equipment under the Coordinating European Council (CEC) F-06-A-96 method, which is very similar to the ASTM D 6079 method, but embodies additional controls on temperature and humidity, and may therefore be expected to provide greater test precision than ASTM D 6079.

The term "cavitation" as used herein means the rapid formation and collapse of vapour pockets in a liquid in regions of locally fluctuating pressure.

Without wishing to be bound by theory it is believed that the film-forming additive may inhibit and/or prevent cavitation according to the present invention in one or more of the following ways.

The film-forming additive may provide a sacrificial layer on the surface of the components exposed to cavitation, such that material is removed from the sacrificial layer rather than from the metallic surface covered and protected by the sacrificial layer

of film-forming additive.

Replenishment of the sacrificial layer may be provided by the supply of fresh additised fuel according to the present invention to the potentially wearing components. Protection  
5 for the metal surfaces of vulnerable components by the sacrificial layer may prevent wear debris from forming and circulating, for example within the injector pump. Furthermore, since the film-forming additive does not itself create abrasive particles, removal of parts of the protective sacrificial layer of film-forming additive by the process of cavitation will not subsequently lead to accelerated wear within diesel engine fuel systems and in  
10 particular within fuel pumps. Therefore use of a film-forming additive according to the present invention may provide protection from the effects of cavitation resulting from the inclusion of a fuel alcohol in diesel as typified by blends such as Ediesel.

Alternatively, or additionally, the existence of a protective film at the metal surface,  
15 whether monolayer or (particularly) multilayer may preclude the possibility of vapour-filled bubble formation in the vicinity of that surface. Fuel alcohols, in particular ethanol, are known to have limited solubility in diesel fuel. The fuel alcohol may thus have a limited solubility in the boundary layer film, which itself is highly compatible with diesel fuel. Further, higher concentrations of fuel alcohol in diesel are typically obtained using  
20 surfactant co-additives. In such cases the fuel alcohol may be thought of as maintained as a suspension of droplets sheathed by surfactant co-additive. On the molecular scale, these can be large assemblies and so physically unable to penetrate any protective film. Thus, the volatile component associated with the onset of cavitation may be physically separated from the metal surface. Vapour-filled bubbles formed during cavitation may  
25 similarly form remote from the surface and so not remove material from it either by plucking or jetting mechanisms.

A further alternative or additional effect according to the present invention, may be the passivating of freshly-exposed surfaces. Cavitation by ultrasound is well-known for  
30 cleaning of metal and other hard surfaces. Enhanced chemical reactivity of metals towards organic species under the influence of power ultrasound is well-known and frequently ascribed to removal of passivating surface oxide or insoluble reaction products. Ediesel and other alcohol-containing diesel fuel blends are widely understood to be more corrosive towards fuel delivery systems than the diesel base fuels. Thus  
35 cavitation can lead to exposure of fresh, highly-reactive metal surface to the alcohol

containing fuel. The films formed on the metal surface may thus prevent access of the corrosive components to the freshly-exposed surface, and thereby reduce or prevent corrosion.

- 5 In yet a further alternative or additional effect, the mechanical grinding action of wear particles within the boundary layer is thought to be responsible for at least some additional wear. Film-forming substances may form films on both the residual surface and the wear particle and so provide boundary lubrication layers on both bodies. This may act to keep the wear-particle in suspension and so ultimately remove it from the  
10 metal surface, or at the least act as a lubricant film to prevent scuffing or other wear.

For ease of reference these and further aspects of the present invention are now discussed under appropriate section headings. However, the teachings under each section are not necessarily limited to each particular section.

15

## PREFERRED EMBODIMENTS

- As previously mentioned, in one aspect, the present invention provides a fuel composition comprising a fuel and a film-forming additive wherein the fuel comprises  
20 diesel and a fuel alcohol and wherein the film-forming additive is present in the fuel composition in an amount of less than 0.1 wt%.

- As previously mentioned, in a further aspect, the present invention provides use of a film-forming additive for inhibiting and/or preventing cavitation in a fuel and/or reducing the  
25 effects of cavitation in a fuel, wherein the fuel comprises diesel and a fuel alcohol.

In a preferred aspect, the film-forming additive is present in an amount of less than 0.01wt%.

- 30 The film-forming additive may be employed at treat rates of up to or less than 0.1 wt%, such as up to or less than 0.08 wt%, such as up to or less than 0.07 wt%, such as up to or less than 0.05 wt%, such as up to or less than 0.04 wt%, such as up to or less than 0.03 wt%, such as up to or less than 0.02 wt%, such as up to or less than 0.01 wt%, preferred treat rates being 10-1,000 ppm e.g. 800 ppm. Particularly preferred treat rates  
35 are 50-500 ppm and most preferred 100-300 ppm. In all cases ppm refers to mg film-



forming additive per kg fuel.

## **FUEL**

- 5 As previously mentioned, the fuel comprises diesel and a fuel alcohol.

### **Fuel Alcohol**

- 10 Preferably the fuel alcohol is present in the fuel in an amount of 1 to 30% by volume, preferably 1 to 20%, such as 1 to 15%, 2 to 15% or 3 to 15%.

Preferably the fuel alcohol is an aliphatic alcohol.

- 15 Preferably the fuel alcohol is an alkanol comprising an alkyl group and a hydroxy group. More preferably the fuel alcohol is an alkanol comprising a linear alkyl group and a hydroxy group.

- 20 Preferably the fuel alcohol is a C<sub>1</sub>-C<sub>20</sub> alcohol such as a C<sub>1</sub>-C<sub>15</sub> alcohol or a C<sub>1</sub>-C<sub>10</sub> alcohol. Preferably the fuel alcohol is a C<sub>1</sub>-C<sub>5</sub> alcohol such as an alcohol selected from methanol, ethanol, propanol and iso-propanol.

In a particularly preferred aspect the fuel alcohol is ethanol.

- 25 Preferably the ethanol is distilled prior to blending with the diesel. The ethanol used is typically, but not by way of limitation, at least 90% preferably 95% and even more preferably at least 96% anhydrous ethanol.

### **Additional Components**

- 30 The fuel composition may additionally comprise one or more additives. Examples of such additives include surfactants such as emulsifiers, stabilising additives and co-solvents.

- 35 The inclusion in the fuel of fuel alcohol, which may not be anhydrous, may typically result in the inclusion of water and it is well known that an additional minor component may be

added to the fuel blend as a co-solvent to stabilise the blend of fuel alcohol and diesel fuel. Without such a component, under certain conditions water is prone to separate out and the alcohol to partition between aqueous and fuel phases.

## 5 Co-solvent

In one preferred aspect the fuel further comprises a co-solvent.

10 A suitable co-solvent may be selected from the group consisting of alkyl alcohols having a hydrocarbon chain length of about three to about six, inclusive, such as tertiary butyl alcohol, for example; naphtha;  $\gamma$ -valerolactone; kerosene; hydrocarbons having a chain length of greater than about 50; and mixtures thereof.

15 Preferably the co-solvent is an alcohol. More preferably the co-solvent has the formula  $R^1O(CH_2CH_2O)_nH$ , wherein  $n$  is a number from 0 to 10 and  $R^1$  is a  $C_{1-30}$  hydrocarbyl group.

20 As used herein, the term "hydrocarbyl" refers to a group comprising at least C and H that may optionally comprise one or more other suitable substituents. Examples of such substituents may include halo-, alkoxy-, nitro-, an alkyl group, or a cyclic group. In addition to the possibility of the substituents being a cyclic group, a combination of substituents may form a cyclic group. If the hydrocarbyl group comprises more than one C then those carbons need not necessarily be linked to each other. For example, at least two of the carbons may be linked *via* a suitable element or group. Thus, the hydrocarbyl group may contain heteroatoms. Suitable heteroatoms will be apparent to those skilled in the art and include, especially nitrogen and oxygen.

In a preferred aspect,  $R^1$  is a hydrocarbon group.

30 As used herein the term "hydrocarbon" means any one of an alkyl group, an alkenyl group, an alkynyl group and an acyl group, which groups may be linear, branched or cyclic, or an aryl group. The term hydrocarbon also includes those groups but wherein they have been optionally substituted. If the hydrocarbon is a branched structure having substituent(s) thereon, then the substitution may be on either the hydrocarbon backbone or on the branch; alternatively the substitutions may be on the hydrocarbon backbone

35

and on the branch.

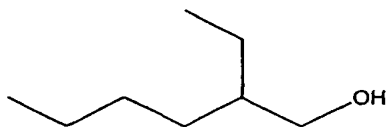
In a highly preferred aspect,  $R^1$  is an alkyl group. In this aspect,  $R^1$  may be linear or branched. In this aspect,  $R^1$  may be saturated or unsaturated.

5

Preferably  $n$  is a number from 0 to 5. In one preferred aspect,  $n$  is 0. In another preferred aspect,  $n$  is a number from 2 to 4, preferably a number from 2 to 3, more preferably  $n$  is about 2.75.

10 In one embodiment, the co-solvent is  $R^1O(CH_2CH_2O)_nH$  wherein  $n$  is 0.

In this embodiment preferably  $R^1$  is a  $C_5$  to  $C_{15}$  alkyl, preferably  $C_5$  to  $C_{10}$  alkyl, more preferably  $C_8$  alkyl. One preferred co-solvent is 2-ethylhexanol:



15

In another embodiment, the co-solvent is  $R^1O(CH_2CH_2O)_nH$  wherein  $n$  is greater than 0.

Preferred co-solvents are alkoxyated alcohols, preferably ethoxylated alcohols. It is highly preferable that the ethoxylated alcohols are oil soluble alcohols. Therefore, alkanols are preferred and these may be primary, secondary or tertiary alkanols and especially primary alkanols. As the oil solubility of the alcohol may vary with the carbon chain length of the ethoxylated alkanol, the alkanol is preferably a  $C_5$  to  $C_{22}$  alkanol, more preferably  $C_5$  to  $C_{15}$  alkanol. The ethoxylated alcohol may comprise a mixture of alkanols. However, it is preferred that in such mixtures one alkanol will predominate. Thus, the most preferred alkanol is predominantly a  $C_9$  to  $C_{15}$  alkanol. In addition the degree of ethoxylation of the alcohol may be varied and the oil solubility will, generally, decrease with the increase in the degree of ethoxylation. It is preferred that the ethoxylate to alcohol ratio is greater than 2. More preferably, the ethoxylate to alcohol ratio is from between 1 and 10, preferably between 1 and 5, more preferably between 1 and 3 and especially between 2 and 3. A commercially available ethoxylated alcohol is especially preferred in which the ethoxylate to alcohol ratio is 2.75. Such an alcohol ethoxylate is available as NEODOL 91/2.5.

12.

Thus, in this preferred embodiment, the co-solvent is  $R^1O(CH_2CH_2O)_nH$  wherein  $n$  is a number from 2 to 4, preferably a number from 2 to 3, more preferably  $n$  is about 2.75. In this embodiment, preferably  $R^1$  is a  $C_5$  to  $C_{15}$  alkyl.

## 5 Surfactant

In another preferred aspect the fuel further comprises a surfactant. Preferably the surfactant is an emulsifier.

10 Examples of suitable surfactants include

- amides of long-chain ( $C_{10}$ - $C_{30}$ ) fatty acids prepared from dialkylaminoalcohols such as dimethylaminoethanol as exemplified in US-A-4,451,265;
- Ammonium salts prepared by reaction of long chain fatty acids with lower trialkylamines as set out in US-A-4,451,267;
- 15 • diesel soluble ethylene oxide/styrene block copolymers, coupled by styrene/butadiene as in US-A-4,482,666;
- 1:2:3 mixtures of sorbitan sesquioleate, polyethylene glycol monooleate and nonylphenol ethoxylate as claimed in WO-A-97/34969;
- reaction product of phthallic (or other monobasic carboxylic) acid + poly(amine) +  
20 second carboxylic acid in the ratio 1/no. of equivalents of first acid: 2/no. of amine groups of polyamine:1/no. of equivalents of second acid as exemplified by EP-A-0386550;
- 93-97% sorbitan fatty acid monoester and 3-7 wt% polysorbate 80 as found in AU 563,404;
- 25 • oleyldiethanolamide, diethanolamine and diethanolamine soap of oleic acid which has been treated with about 0-7½ of oleic acid as discussed in US-A-4,173,455; and
- $C_8$ - $C_{22}$  fatty acids as polyglycerol esters, sorbitan esters or diacetyl tartaric acid esters of glycerol esters of the said fatty acids as discussed in DE 2,229,918.

30

In a preferred aspect, the surfactant has the formula  $R^2(CO)_m-N([CH_2]_{1-10}OH)_2$  wherein  $m$  is 0 or 1 and  $R^2$  is a  $C_{1-30}$  hydrocarbyl group.

In a preferred aspect, the surfactant has the formula  $R^2(CO)_m-N([CH_2]_{1-5}OH)_2$  wherein  $m$   
35 is 0 or 1 and  $R^2$  is a  $C_{1-30}$  hydrocarbyl group.

In a preferred aspect, the surfactant has the formula  $R^2(CO)_m-N([CH_2]_{1-3}OH)_2$  wherein m is 0 or 1 and  $R^2$  is a  $C_{1-30}$  hydrocarbyl group.

- 5 In a preferred aspect, the surfactant has the formula  $R^2(CO)_m-N(CH_2CH_2OH)_2$  wherein m is 0 or 1 and  $R^2$  is a  $C_{1-30}$  hydrocarbyl group.

Preferably  $R^2$  is a hydrocarbon group. More preferably  $R^2$  is an alkyl group or an alkenyl group. In this aspect,  $R^2$  may be linear or branched. In this aspect,  $R^2$  may be saturated  
10 or unsaturated.

Preferably  $R^2$  is a  $C_{8-22}$  hydrocarbyl group, more preferably a  $C_{8-22}$  hydrocarbon group, such as a  $C_{8-22}$  alkyl group or a  $C_{8-22}$  alkenyl group.

- 15 Preferably  $R^2$  is a  $C_{10-20}$  hydrocarbyl group, more preferably a  $C_{10-20}$  hydrocarbon group, such as a  $C_{10-20}$  alkyl group or a  $C_{10-20}$  alkenyl group.

Preferably  $R^2$  is a  $C_{12-20}$  hydrocarbyl group, more preferably a  $C_{12-20}$  hydrocarbon group, such as a  $C_{12-20}$  alkyl group or a  $C_{12-20}$  alkenyl group.

20

Preferably  $R^2$  is a  $C_{12-20}$  hydrocarbyl group, more preferably a  $C_{14-18}$  hydrocarbon group, such as a  $C_{14-18}$  alkyl group or a  $C_{14-18}$  alkenyl group.

- In one embodiment, m is 0. Thus the surfactant has a formula  $R^2N([CH_2]_{1-10}OH)_2$ ,  
25 preferably  $R^2N([CH_2]_{1-5}OH)_2$ , preferably  $R^2N([CH_2]_{1-3}OH)_2$ , preferably  $R^2N(CH_2CH_2OH)_2$  wherein  $R^2$  is a  $C_{1-30}$  hydrocarbyl group. In this aspect, preferably  $R^2$  is a  $C_{8-22}$  hydrocarbon, such as a  $C_{16-20}$  hydrocarbon, more preferably a  $C_{18}$  hydrocarbon. In this aspect, preferably  $R^2$  is unsaturated, more preferably  $R^2$  is an alkenyl. Preferably  $R^2$  is an unsaturated  $C_{18}$  hydrocarbon, more preferably a  $C_{18}$  alkenyl, most preferably an oleyl  
30 group.

- In another embodiment m is 1. Thus the surfactant has a formula  $R^2(CO)-N([CH_2]_{1-10}OH)_2$ , preferably  $R^2(CO)-N([CH_2]_{1-5}OH)_2$ , preferably  $R^2(CO)-N([CH_2]_{1-3}OH)_2$ , preferably  $R^2(CO)-N(CH_2CH_2OH)_2$  wherein  $R^2$  is a  $C_{1-30}$  hydrocarbyl group. In this aspect,  
35 preferably  $R^2$  is a  $C_{7-21}$  hydrocarbon, such as a  $C_{15-19}$  hydrocarbon, more preferably a  $C_{17}$

hydrocarbon. In this aspect  $R^2$  may be saturated or unsaturated. Preferably  $R^2$  is a  $C_{7-21}$  alkyl, such as a  $C_{15-19}$  alkyl, more preferably a  $C_{17}$  alkyl.

### Co-solvent/Surfactant Systems

5

In a highly preferred aspect, the fuel further comprises a co-solvent and a surfactant.

In one preferred aspect, the fuel further comprises a co-solvent of formula  $R^1O(CH_2CH_2O)_nH$  wherein  $n$  is 0 and  $R^1$  is ethylhexyl; and a surfactant of formula  
10  $R^2(CO)_m-N(CH_2CH_2OH)_2$  wherein  $R^2$  is a  $C_{18}$  alkenyl and  $m$  is 0.

Preferably the fuel further comprises 2-ethylhexanol and a surfactant of formula  $R^2N(CH_2CH_2OH)_2$  wherein  $R^2$  is an oleyl group.

15 In another preferred aspect, the fuel further comprises a co-solvent of formula  $R^1O(CH_2CH_2O)_nH$  wherein  $n$  is from 2 to 3 and  $R^1$  is a  $C_5$  to  $C_{15}$  alkyl; and a surfactant of formula  $R^2(CO)_m-N(CH_2CH_2OH)_2$  wherein  $R^2$  is a saturated or unsaturated  $C_{17}$  hydrocarbon and  $m$  is 1.

20 Preferably the fuel further comprises a co-solvent of formula  $R^1O(CH_2CH_2O)_nH$  wherein  $n$  is about 2.75 and  $R^1$  is a  $C_5$  to  $C_{15}$  alkyl; and a surfactant of formula  $R^2(CO)-N(CH_2CH_2OH)_2$  wherein  $R^2$  is a  $C_{17}$  alkyl.

Preferred surfactant systems include  $C_8$ - $C_{22}$  acid diethanolamides, e.g.  $C_{12}$  acid  
25 diethanolamides, preferably  $C_{18}$  diethanolamide and fatty acid ethoxylates of  $C_8$ - $C_{22}$  acids, e.g.  $C_{12}$ , preferably  $C_{18}$  with 1-12, preferably 2-10, most preferably about 7 ethoxy groups. A particularly preferred system is 1:1:2 mixture of these two components with the preferred alcohol ethoxylate cosolvent.

30 It will be readily understood that when a co-solvent is present, the co-solvent is different from the film-forming additive.

It will be readily understood that when a surfactant is present, the surfactant is different from the film-forming additive.

35

It will be readily understood that when a co-solvent and a surfactant are present, the co-solvent is different from the surfactant.

The co-solvent is typically present in an amount of more than 0.1wt%. The surfactant is typically present in an amount of more than 0.1wt%.

### **FILM-FORMING ADDITIVE**

In one aspect, the film-forming additive comprises a functional group selected from the group consisting of a carboxylic acid, a carboxylic ester, an alcohol, an amide and an amine.

Preferably, the film-forming additive comprises a functional group selected from the group consisting of a carboxylic acid, a carboxylic ester and an alcohol.

In one embodiment, preferably the film-forming additive comprises a carboxylic acid.

In one embodiment, preferably the film-forming additive comprises a carboxylic ester group.

In one embodiment, preferably the film-forming additive comprises an alcohol group.

Preferably, the film-forming additive comprises a carboxylic ester group and an alcohol group.

In a preferred aspect, the film-forming additive is one or more compounds selected from the group consisting of (a) a C<sub>5</sub>-C<sub>100</sub> hydrocarbyl substituted with at least one carboxylic acid group; (b) the reaction product of a C<sub>5</sub>-C<sub>100</sub> hydrocarbyl substituted with at least one carboxylic acid group or comprising at least one carboxylic anhydride group with (i) a reactive alcohol; and/or (ii) an amine; and/or (iii) an alcohol-amine; and/or (iv) an amino acid; (c) a polymeric hydrocarbyl substituted with a hydroxy group and/or substituted with a group comprising a nitrogen; and (d) an aromatic ring system substituted with a hydroxy group and/or substituted with a group comprising an amine and optionally substituted with a hydrocarbon group.

As used herein, the term "hydrocarbyl" refers to a group comprising at least C and H that may optionally comprise one or more other suitable substituents. Examples of such substituents may include halo-, alkoxy-, nitro-, an alkyl group, or a cyclic group. In addition to the possibility of the substituents being a cyclic group, a combination of  
5 substituents may form a cyclic group. If the hydrocarbyl group comprises more than one C then those carbons need not necessarily be linked to each other. For example, at least two of the carbons may be linked *via* a suitable element or group. Thus, the hydrocarbyl group may contain heteroatoms. Suitable heteroatoms will be apparent to those skilled in the art and include, especially nitrogen and oxygen.

10

In one aspect preferably the hydrocarbyl group is free of sulphur.

As used herein the term "hydrocarbon" means any one of an alkyl group, an alkenyl group, an alkynyl group and an acyl group, which groups may be linear, branched or  
15 cyclic, or an aryl group. The term hydrocarbon also includes those groups but wherein they have been optionally substituted. If the hydrocarbon is a branched structure having substituent(s) thereon, then the substitution may be on either the hydrocarbon backbone or on the branch; alternatively the substitutions may be on the hydrocarbon backbone and on the branch.

20

**(a) C<sub>5</sub>-C<sub>100</sub> Hydrocarbyl and (b) Reaction Product of C<sub>5</sub>-C<sub>100</sub> Hydrocarbyl**

Preferably, the film-forming additive is one or more compounds selected from the group consisting of (a) a C<sub>5</sub>-C<sub>100</sub> hydrocarbyl substituted with at least one carboxylic acid group;  
25 and (b) the reaction product of a C<sub>5</sub>-C<sub>100</sub> hydrocarbyl substituted with at least one carboxylic acid group or comprising at least one carboxylic anhydride group with (i) a reactive alcohol; and/or (ii) an amine; and/or (iii) an alcohol-amine; and/or (iv) an amino acid.

30 C<sub>5</sub>-C<sub>100</sub> Hydrocarbyl

Preferably the C<sub>5</sub>-C<sub>100</sub> hydrocarbyl is a C<sub>5</sub>-C<sub>80</sub> hydrocarbyl group such as a C<sub>5</sub>-C<sub>50</sub> group, a C<sub>5</sub>-C<sub>40</sub> group or a C<sub>5</sub>-C<sub>30</sub> group. More preferably the C<sub>5</sub>-C<sub>100</sub> hydrocarbyl is a C<sub>5</sub>-C<sub>20</sub> group such as a C<sub>10</sub>-C<sub>20</sub> group or a C<sub>12</sub>-C<sub>18</sub> group in particular a C<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub>, or C<sub>18</sub> group.

35



Preferably the  $C_5$ - $C_{100}$  hydrocarbyl is aliphatic, more preferably it is a  $C_5$ - $C_{100}$  hydrocarbon, more preferably a  $C_5$ - $C_{100}$  alkyl or alkenyl.

According to one preferred embodiment, the  $C_5$ - $C_{100}$  hydrocarbyl substituted with at least one carboxylic acid group comprises a terminal carboxylic acid group.

In this aspect, preferably the  $C_5$ - $C_{100}$  hydrocarbyl substituted with at least one carboxylic acid group is linear.

In this aspect, preferably the  $C_5$ - $C_{100}$  hydrocarbyl substituted with at least one carboxylic acid group is selected from the group consisting of lauric, myristic, myristoleic, palmitic, palmitoleic, stearic, elaidic, oleic and linoleic acid.

Examples of suitable compounds include natural and synthetic fatty acids as well as the mixtures and impure fractions thereof such as tall-oil fatty acids, tallow oils, palm oil, rape-seed oil and the like.

According to another preferred embodiment, the  $C_5$ - $C_{100}$  hydrocarbyl substituted with at least one carboxylic acid group is substituted with at least two carboxylic acid groups.

In this aspect, preferably the  $C_5$ - $C_{100}$  hydrocarbyl substituted with at least two carboxylic acid groups is a dimer-acid.

The term "dimer-acid" as used herein means the dimerisation product of two unsaturated  $C_5$ - $C_{100}$  hydrocarbyls each substituted with at least one carboxylic acid group.

Examples of preferred dimer-acids include the dimerisation products of two linear alkenyl groups each substituted with at least one carboxylic acid group, preferably at least one terminal carboxylic acid group. Particularly preferred is dimerised linoleic acid such as DCI 4A available from The Associated Octel Company, UK.

Alternatively, in this aspect, preferably the  $C_5$ - $C_{100}$  hydrocarbyl substituted with at least two carboxylic acid groups is derived from maleic acid, maleic anhydride, succinic acid, or succinic anhydride.

- Examples of suitable compounds include alkyl- or alkenyl succinic acids. These materials may be formed via the reaction of maleic anhydride with alkenes. Typically, alkenes suitable for use in such reactions are obtained by the oligomerisation of low molecular weight olefin streams, such as ethylene, propylene and butylenes, including both 2-methylpropene and mixed C<sub>4</sub>-monoolefin streams. The double bond in the oligomer may be terminal (vinyl), di- or tri-substituted or may, as is particularly the case for oligomers from the C<sub>4</sub> olefin stream, comprise mixtures thereof. Suitable olefins derived from ethylene include dodec-1-ene, octadec-1-ene and the mixed internal olefins obtained by isomerisation thereof. A suitable olefin derived from propene would be tetrapropene. Suitable olefins derived from C<sub>4</sub>-olefins include the so-called poly(butenes), characterised by their number average molecular weight. An example of a suitable such olefin would be BP-Amoco Indopol L-6, which has a number average molecular weight of 260. The reaction between the olefin and maleic acid may be carried out by the so-called "thermal route" resulting in a succinate substituted at the  $\alpha$ -position to only one carboxyl group or via the "chlorine route" resulting in a succinate substituted  $\alpha$ - to each carboxyl group and comprising part of a six-membered ring structure. The succinates may also be hydrogenated to substantially convert the alkenyl-succinates to alkyl-succinates.
- Preferably the C<sub>5</sub>-C<sub>100</sub> hydrocarbyl comprising at least one carboxylic anhydride group is derived from maleic acid, maleic anhydride, succinic acid, or succinic anhydride.

#### **(b) Reaction Product of C<sub>5</sub>-C<sub>100</sub> Hydrocarbyl**

- In a preferred aspect, the film-forming additive is (b) the reaction product of a C<sub>5</sub>-C<sub>100</sub> hydrocarbyl substituted with at least one carboxylic acid group or comprising at least one carboxylic anhydride group with (i) a reactive alcohol; and/or (ii) an amine; and/or (iii) an alcohol-amine; and/or (iv) an amino acid.
- Preferably the C<sub>5</sub>-C<sub>100</sub> hydrocarbyl substituted with at least one carboxylic acid group or comprising at least one carboxylic anhydride group is as herein described.

- More preferably the C<sub>5</sub>-C<sub>100</sub> hydrocarbyl substituted with at least one carboxylic acid group or comprising at least one carboxylic anhydride group is derived from maleic acid, maleic anhydride, succinic acid or succinic anhydride.

### Reactive Alcohol

The reactive alcohol may be a mono-alcohol, a diol, a triol or a polyol. Preferably the  
5 reactive alcohol is a diol, a triol or a polyol.

More preferably the reactive alcohol is selected from the group consisting of ethylene glycol, propylene glycol, butylene glycol, glycerol, pentaerythritol and oligomers thereof.

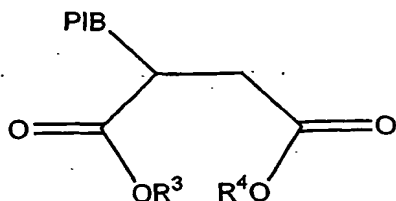
10 In one preferred embodiment, the reactive alcohol is 1-aza-3,7-dioxabicyclo [3.3.0]-oct-5-yl methyl alcohol.

In a preferred aspect the film-forming additive is (b) the reaction product of a C<sub>5</sub>-C<sub>100</sub> hydrocarbyl substituted with at least one carboxylic acid group or comprising at least one  
15 carboxylic anhydride group with (i) a reactive alcohol.

Particularly suitable as a film-forming additive according to the present invention are the esters of mono-, di-, tri- and poly(hydroxy) alcohols with natural and synthetic long chain fatty acids particularly those in which there is an excess of hydroxyl groups to carboxylic  
20 acid groups. For example, a diol may be reacted with a mono-carboxylic acid to provide products containing in excess of two molecules of acid per molecule of alcohol, up to the theoretical maximum of one acid per alcohol.

Various esters of the succinates as previously described are also suitable as film-forming  
25 additives according to the present invention. For example the hemi-esters with mono-alcohols, such as in particular propan-2-ol, or with polyhydric alcohols as herein described. Alternatively, mixed-esters of the above succinates with a mono-alcohol and a polyhydric alcohol may be used. For example, a succinate ester of propan-2-ol with ethylene glycol. Finally, the esters of succinates as described above with poly(hydric)  
30 alcohols may be used.

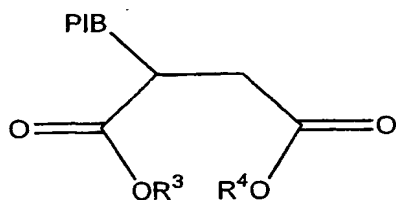
In a preferred aspect the film-forming additive is a compound of formula



wherein PIB is a polyisobutene group having an average molecular weight of from 200 to 1000 and  $R^3$  and  $R^4$  are independently selected from (C1-10 straight or branched alkyl)-OH, and H with the proviso that  $R^3$  and  $R^4$  are not both H.

5

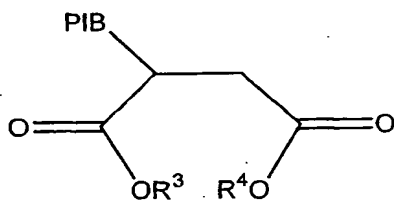
In a preferred aspect the film-forming additive is a compound of formula



wherein PIB is a polyisobutene group having an average molecular weight of from 200 to 1000 and  $R^3$  and  $R^4$  are independently selected from (C1-5 straight or branched alkyl)-OH, and H with the proviso that  $R^3$  and  $R^4$  are not both H.

10

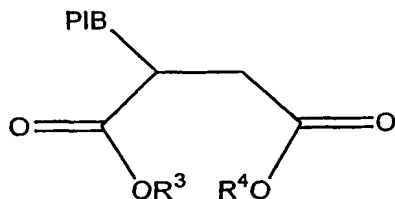
In a preferred aspect the film-forming additive is a compound of formula



wherein PIB is a polyisobutene group having an average molecular weight of from 200 to 1000 and  $R^3$  and  $R^4$  are independently selected from (C1-3 straight or branched alkyl)-OH, and H with the proviso that  $R^3$  and  $R^4$  are not both H.

15

In a preferred aspect the film-forming additive is a compound of formula



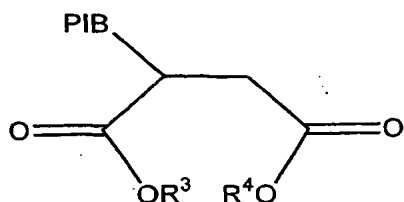
wherein PIB is a polyisobutene group having an average molecular weight of from 200 to 1000 and  $R^3$  and  $R^4$  are independently selected from  $-\text{CH}_2\text{CH}_2\text{OH}$ ,  $-\text{CH}(\text{CH}_3)_2$ , and H

20

21

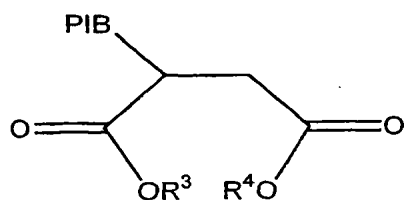
with the proviso that  $R^3$  and  $R^4$  are not both H.

In a preferred aspect the film-forming additive is a compound of formula



- 5 wherein PIB is a polyisobutene group having an average molecular weight of from 200 to 1000 and  $R^3$  and  $R^4$  are independently selected from (C1-10 straight or branched alkyl)-OH, and H with the proviso that  $R^3$  and  $R^4$  are not both H.

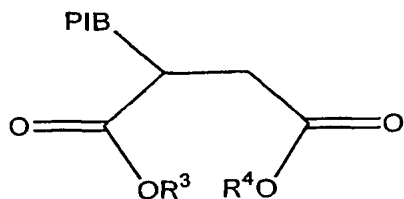
In a preferred aspect the film-forming additive is a compound of formula



10

- wherein PIB is a polyisobutene group having an average molecular weight of from 200 to 800 and  $R^3$  and  $R^4$  are independently selected from (C1-10 straight or branched alkyl)-OH, and H with the proviso that  $R^3$  and  $R^4$  are not both H.

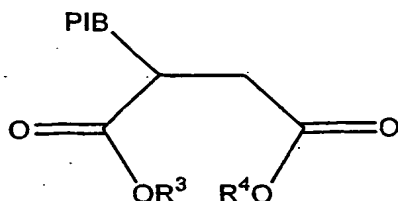
- 15 In a preferred aspect the film-forming additive is a compound of formula



- wherein PIB is a polyisobutene group having an average molecular weight of from 200 to 600 and  $R^3$  and  $R^4$  are independently selected from (C1-10 straight or branched alkyl)-OH, and H with the proviso that  $R^3$  and  $R^4$  are not both H.

20

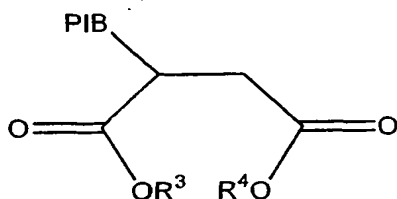
In a preferred aspect the film-forming additive is a compound of formula



wherein PIB is a polyisobutene group having an average molecular weight of from 200 to 400 and R<sup>3</sup> and R<sup>4</sup> are independently selected from (C1-10 straight or branched alkyl)-OH, and H with the proviso that R<sup>3</sup> and R<sup>4</sup> are not both H.

5

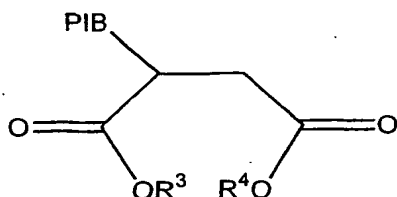
In a preferred aspect the film-forming additive is a compound of formula



wherein PIB is a polyisobutene group having an average molecular weight of from 200 to 300 and R<sup>3</sup> and R<sup>4</sup> are independently selected from (C1-10 straight or branched alkyl)-OH, and H with the proviso that R<sup>3</sup> and R<sup>4</sup> are not both H.

10

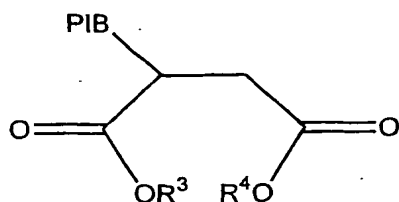
In a highly preferred aspect the film-forming additive is a compound of formula



wherein PIB is a polyisobutene group having an average molecular weight of from 200 to 1000 and R<sup>3</sup> and R<sup>4</sup> are independently selected from -CH<sub>2</sub>CH<sub>2</sub>OH, -CH(CH<sub>3</sub>)<sub>2</sub>, and H with the proviso that R<sup>3</sup> and R<sup>4</sup> are not both H.

15

In a highly preferred aspect the film-forming additive is a compound of formula

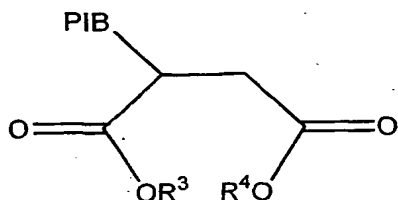


wherein PIB is a polyisobutene group having an average molecular weight of from 200 to 800 and R<sup>3</sup> and R<sup>4</sup> are independently selected from -CH<sub>2</sub>CH<sub>2</sub>OH, -CH(CH<sub>3</sub>)<sub>2</sub>, and H with

20

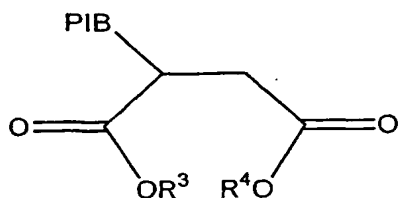
the proviso that  $R^3$  and  $R^4$  are not both H.

In a highly preferred aspect the film-forming additive is a compound of formula



- 5 wherein PIB is a polyisobutene group having an average molecular weight of from 200 to 600 and  $R^3$  and  $R^4$  are independently selected from  $-\text{CH}_2\text{CH}_2\text{OH}$ ,  $-\text{CH}(\text{CH}_3)_2$ , and H with the proviso that  $R^3$  and  $R^4$  are not both H.

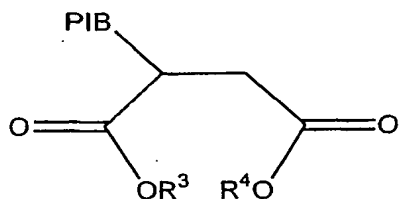
In a highly preferred aspect the film-forming additive is a compound of formula



10

- wherein PIB is a polyisobutene group having an average molecular weight of from 200 to 400 and  $R^3$  and  $R^4$  are independently selected from  $-\text{CH}_2\text{CH}_2\text{OH}$ ,  $-\text{CH}(\text{CH}_3)_2$ , and H with the proviso that  $R^3$  and  $R^4$  are not both H.

- 15 In a highly preferred aspect the film-forming additive is a compound of formula

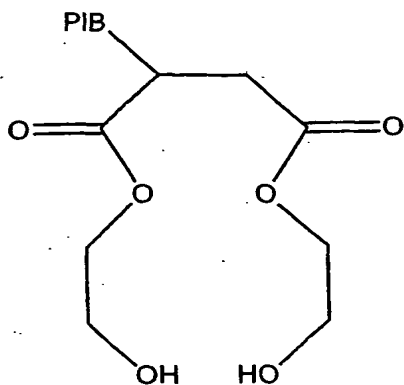


- wherein PIB is a polyisobutene group having an average molecular weight of from 200 to 300 and  $R^3$  and  $R^4$  are independently selected from  $-\text{CH}_2\text{CH}_2\text{OH}$ ,  $-\text{CH}(\text{CH}_3)_2$ , and H with the proviso that  $R^3$  and  $R^4$  are not both H.

20

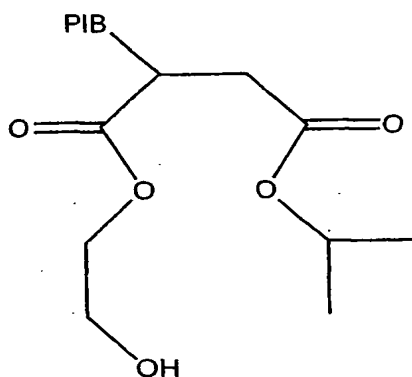
- In one preferred embodiment,  $R^3$  and  $R^4$  are both  $-\text{CH}_2\text{CH}_2\text{OH}$  and the film-forming additive is a compound of formula

24.

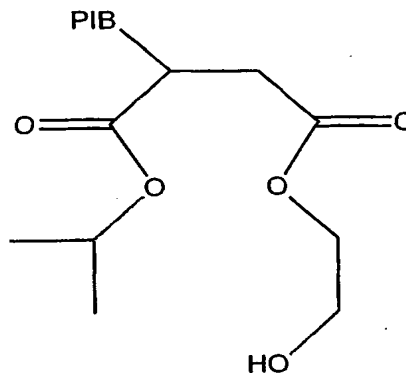


In another preferred embodiment one of  $R^3$  and  $R^4$  is  $-\text{CH}_2\text{CH}_2\text{OH}$  and the other is  $-\text{CH}(\text{CH}_3)_2$  and the film-forming additive is a compound of formula

5



or



or a mixture thereof.

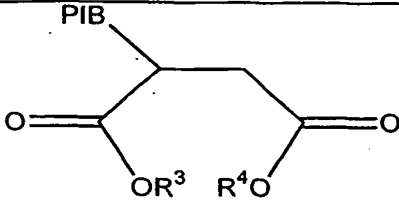
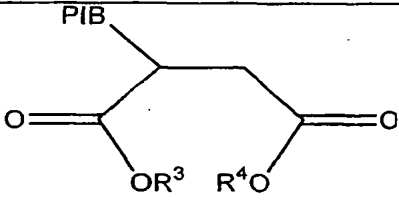
In a preferred aspect PIB is a polyisobutene group having an average molecular weight of about 260.

10

Further preferred film-forming additives are

Additive	
1	Dimerised linoleic acid
2	<p>PIB is a poly(butene) of number average</p>



	<p>molecular weight 260,  <math>R^3</math> and <math>R^4</math> are both <math>-\text{CH}_2\text{CH}_2\text{OH}</math>.</p>
3	<p>  </p> <p>PIB is a poly(butene) of number average molecular weight 260  <math>R^3</math> and <math>R^4</math> are each independently <math>-\text{CH}_2\text{CH}_2\text{OH}</math> or <math>-\text{CH}(\text{CH}_3)_2</math> and are in substantially 1:1 molar ratio overall.</p>
4	<p>  </p> <p>PIB is a poly(butene) of number average molecular weight 260  one of <math>R^3</math> and <math>R^4</math> is H or <math>-\text{CH}(\text{CH}_3)_2</math> and the other of <math>R^3</math> and <math>R^4</math> is H, <math>-\text{CH}(\text{CH}_3)_2</math> or <math>-\text{CH}_2\text{CH}_2\text{OH}</math>,  provided that <math>R^3</math> and <math>R^4</math> are not both H.</p>

### Amine

The amine may be any suitable substituted or unsubstituted amine. If the amine is substituted it may typically be substituted with a hydrocarbon group, preferably an alkyl group. However, examples of suitable substituted amines include guanidine, aminoguanidine, urea, thiourea and salts thereof.

Suitable amines also include polyamines and poly(piperidine).

10

### Alcohol-amine

The alcohol-amines which are particularly suitable include secondary alcohol-amines for

example aminoethyl ethanolamine and polyhydric alcohol-amines such as di-alkanolamines, in particular di-ethanolamine; and primary alcohol-amines.

#### Amino Acid

Preferably the amino-acid is a primary amino acid. More preferably the amino acid is a  $\alpha,\omega$ -primary amino-acid.

#### Reactions

The reactions with (i) a reactive alcohol; and/or (ii) an amine; and/or (iii) an alcohol-amine; and/or (iv) an amino acid may be carried out stepwise or alternatively the reactions may be carried out simultaneously in a single reaction vessel. If the reactions are carried out stepwise they may be carried out in any order.

Examples of suitable film-forming additives according to this aspect of the present invention include amides or mixtures of ester and amide which may be prepared by reaction of any of the above-described carboxylic or succinic anhydrides, acids or hemi-esters with poly(hydric) alcohol-amines, such as, for example, di-ethanolamine.

Also suitable are mixed amides of the succinates which may be prepared by stepwise reaction of the succinic anhydride or succinic acid with secondary amine or secondary alcohol-amines followed by poly(amine), poly(piperidine) or alkoxyamine. The stepwise reactions may be carried out in any order.

Succinates prepared as herein described may also be converted into succinimides of utility in the current application by reaction with alcohol-amines containing at least one primary amine group.

Alkyl or alkenyl succinates, prepared as outlined above, may be converted to imido-acids by reaction with primary amino-acid, especially  $\alpha,\omega$ -primary amino-acids. Species useful in the current application may then be obtained by further reaction with alcohol-amines, such as diethanolamine or aminoethyl ethanolamine to yield mixed esters and amides of the succinic imino-acid.

In a further broad aspect, where sulphur-content of the film-forming additive is not an issue, sulfonyl and sulfinyl species may be used. Thus, sulfanoyl dialkanoyl esters of carboxylic or succinic acids, alkanoyl hemi-esters or hemi-amides may be employed. Alternatively, hydrocarbyl sulfonyl or sulfinyl alkanols or N-aliphatic hydroxycarbyl  
5 hydroxyalkyl sulfinyl or sulfonyl succinimides may be used.

### (c) Polymeric Hydrocarbyl

As previously mentioned, in one preferred aspect the film-forming additive of the present  
10 invention is (c) a polymeric hydrocarbyl substituted with a hydroxy group and/or substituted with a group comprising a nitrogen.

Preferably the polymeric hydrocarbyl is a polymer of C<sub>2</sub>-C<sub>10</sub> hydrocarbon monomers, such as C<sub>2</sub>-C<sub>8</sub> monomers, C<sub>2</sub>-C<sub>6</sub> monomers or C<sub>2</sub>-C<sub>4</sub> monomers.  
15

Preferably the polymeric hydrocarbyl is a polymeric hydrocarbon.

Examples of suitable polymeric hydrocarbyls include the olefin oligomerisation products obtained by the oligomerisation of low molecular weight olefin streams, such as ethylene, propylene and butylenes, including both 2-methylpropene and mixed C<sub>4</sub>-monoolefin  
20 streams.

In one embodiment preferably the polymeric hydrocarbyl is a primary alcohol.

25 Examples of suitable film-forming additives according to this aspect are primary linear alcohols such as those prepared from the various ethylene oligomerisation processes, for example aluminium alkyls-based procedures.

In one embodiment preferably the polymeric hydrocarbyl is substituted with a group  
30 comprising an amide group.

Suitable polymeric hydrocarbyls substituted with a group comprising an amide group may be obtained from polymeric hydrocarbyls in the following manner. The polymeric hydrocarbyls may be aminated, whether directly, by formylation followed by reductive  
35 amination or reaction with acrylonitrile followed by reduction. Formamides of such

amines may be employed. Alternatively, such amines may be reacted with acetoacetamides or N-substituted acetoacetamides to yield alkyl imino acetamides or N-substituted alkyl imino acetamides. Further, hydroxyacetamides, formed by reaction of primary ether amine with a hydroxycarboxylic acid, such as glycolic acid, may be used.

5

#### (d) Aromatic Ring System

As previously mentioned, in one preferred aspect the film-forming additive of the present invention is (d) an aromatic ring system substituted with a hydroxy group and/or substituted with a group comprising an amine and optionally substituted with a hydrocarbon group.

Examples of suitable film-forming additives in this aspect include hydroxylated polycyclic heteroaromatic species such as 8-hydroxyquinoline and polyhydric polycyclic aromatic species, such as 2,3-dihydroxynaphthalene.

15

In this aspect preferably the film-forming additive is the product of a Mannich reaction.

Mannich base detergents are formed by reaction of an optionally alkylated or alkenylated phenol with formaldehyde or other aldehyde and an amine. For example, the reaction product of an alcohol-amine, a different diamine or other poly(amine) containing at least one reactive primary or secondary amino group, an aldehyde and an alkyl phenol.

20

#### Mixtures

25

As previously mentioned, in a preferred aspect, the film-forming additive is one or more compounds selected from the group consisting of (a) a C<sub>5</sub>-C<sub>100</sub> hydrocarbyl substituted with at least one carboxylic acid group; (b) the reaction product of a C<sub>5</sub>-C<sub>100</sub> hydrocarbyl substituted with at least one carboxylic acid group or comprising at least one carboxylic anhydride group with (i) a reactive alcohol; and/or (ii) an amine; and/or (iii) an alcohol-amine; and/or (iv) an amino acid; (c) a polymeric hydrocarbyl substituted with a hydroxy group and/or substituted with a group comprising a nitrogen; and (d) an aromatic ring system substituted with a hydroxy group and/or substituted with a group comprising an amine and optionally substituted with a hydrocarbon group.

35

In a preferred embodiment the film-forming additive may comprise more than one compound selected from the group consisting of (a), (b), (c) and (d).

Thus, in one aspect, the film-forming additive comprises (a) a C<sub>5</sub>-C<sub>100</sub> hydrocarbyl substituted with at least one carboxylic acid group; and (d) an aromatic ring system substituted with a hydroxy group and/or substituted with a group comprising an amine and optionally substituted with a hydrocarbon group.

In another aspect, the film-forming additive comprises (b) the reaction product of a C<sub>5</sub>-C<sub>100</sub> hydrocarbyl substituted with at least one carboxylic acid group or comprising at least one carboxylic anhydride group with (i) a reactive alcohol; and/or (ii) an amine; and/or (iii) an alcohol-amine; and/or (iv) an amino acid; and (d) an aromatic ring system substituted with a hydroxy group and/or substituted with a group comprising an amine and optionally substituted with a hydrocarbon group.

In a further aspect, the film-forming additive comprises (a) a C<sub>5</sub>-C<sub>100</sub> hydrocarbyl substituted with at least one carboxylic acid group; (b) the reaction product of a C<sub>5</sub>-C<sub>100</sub> hydrocarbyl substituted with at least one carboxylic acid group or comprising at least one carboxylic anhydride group with (i) a reactive alcohol; and/or (ii) an amine; and/or (iii) an alcohol-amine; and/or (iv) an amino acid; and (d) an aromatic ring system substituted with a hydroxy group and/or substituted with a group comprising an amine and optionally substituted with a hydrocarbon group.

In another aspect, the film-forming additive comprises (a) a C<sub>5</sub>-C<sub>100</sub> hydrocarbyl substituted with at least one carboxylic acid group; (b) the reaction product of a C<sub>5</sub>-C<sub>100</sub> hydrocarbyl substituted with at least one carboxylic acid group or comprising at least one carboxylic anhydride group with (i) a reactive alcohol; and/or (ii) an amine; and/or (iii) an alcohol-amine; and/or (iv) an amino acid; (c) a polymeric hydrocarbyl substituted with a hydroxy group and/or substituted with a group comprising a nitrogen; and (d) an aromatic ring system substituted with a hydroxy group and/or substituted with a group comprising an amine and optionally substituted with a hydrocarbon group.

Examples of useful film-forming additive according to this aspect of the present invention include Mannich base detergents in combination with one or more of an acid, a hemi-ester, an ester, an amide, an amido-ester, an imino or an imido compound. Further, other

dispersant-type molecules such as the PIB-amines or poly(oxyalkylene) amines may be used in combination with the above species. PIB-amines may be prepared from the same olefin sources as described for the formation of alkenyl succinic acids. Typically, higher molecular weight oligomers, e.g. 500 to 1500 amu no. average molecular weight would be employed. The PIB-amine may be prepared by chlorination and reaction with amine or poly(amine) or by hydroformylation then reaction with amine or poly(amine). Poly(alkylene) amines may be formed by oligomerisation of alkylene (typically ethylene, propylene or butylene) oxides initiated by amine or poly(amine).

## 10 PROCESS

As previously mentioned, in one aspect, the present invention provides a process for supplying a fuel composition to a combustion engine wherein the process comprises (i) pumping the fuel composition with a rotary pump to supply the fuel composition to the combustion engine wherein the fuel composition comprises diesel, a fuel alcohol and a film-forming additive.

In a preferred aspect the fuel composition further comprises a co-solvent and/or one or more surfactants.

Preferably the pump supplies the fuel composition to the combustion engine at a rate which under normal design operating conditions would result in cavitation of the pump if operated with a fuel comprising diesel and the fuel alcohol in the absence of the film-forming additive.

Normal design operating conditions are those in which the pump is supplying fuel to the engine at rates sufficient to supply the fuel requirement of the engine at all conditions from idle speed, zero or near-zero load to rated speed (rev/min) at rated power. This requirement may substantially exceed the fuel consumption of the engine as in many designs there is a return of fuel from the engine to the fuel tank. Without wishing to be bound by theory it is believed that a pump is most likely to be subjected to more rapid wear when the engine is operating at or near to rated power.

Preferably the film-forming additive, the fuel and the fuel alcohol are as herein defined.

In a preferred aspect the fuel composition further comprises a co-solvent and/or one or more surfactants.

In a broad aspect, the present invention provides a process for supplying a fuel composition to a combustion engine wherein the process comprises (i) pumping the fuel composition with a pump to supply the fuel composition to the combustion engine wherein the fuel composition comprises diesel, a fuel alcohol and a film-forming additive.

In this aspect preferably the pump is a rotary pump. The pump may, however be another pump such as an "in-line" pump.

## **EXAMPLES**

### **Fuel Lubricity Characteristics**

15

The lubricity of diesel fuel is most conveniently measured by means of the test protocol well known to those skilled in the art as the CEC F-06-A-96 HFRR test. Diesel fuel blends were tested to this method, modified solely in respect of temperature of execution. The standard procedure is executed at 60°C. Because of flash point concerns in blends containing ethanol, the tests were carried out at 25°C. Values for lubricity were established. Some of the diesel fuel blends contained ethanol, together with additional minor components as indicated in the data set contained in Table 2.

25

Table 2 Lubricity characteristics of diesel fuels with and without alcohol

Fuel tested	Wear Scar Diameter, microns
ULSD 3	258
ULSD 3 + Ethanol + Octimax	339
EN 590	237
EN 590 + Ethanol + Octimax	313
Kerosene	732
Kerosene + Ethanol + Octimax	412
Kerosene + Ethanol	745

The minor component described as Octimax is a co-solvent [STEVE –is Octimax

available from a commercial source? Do you know the chemical composition?] used to stabilise the blend of diesel fuel with ethanol. Kerosene does not require the use of a co-solvent, so it was possible to establish the effect of ethanol on lubricity in kerosene independently of the use of the Octimax component.

5

The presence of ethanol in a diesel fuel blend can be seen to increase the wear scar diameter, although the effect is fuel dependent.

10

The significance of the values of wear scar diameter (WSD) obtained, lies in their relationship to wear observed in rotary distributor type diesel injector pumps. It has been established through extensive testing programmes with this type of pump that a WSD value of less than 460 microns is required. This level of lubricity in the HFRR test is commonly believed to prevent accelerated wear in rotary distributor type pumps.

15

#### **Wear in Rotary Distributor Pumps**

20

The test protocol employed to establish wear patterns with rotary distributor pumps is the CEC F-32-x-99 method. This 1000h duration protocol is an accelerated wear test method, which rates components of the injector pump for wear, and as a result indicates the probable acceptable life of the pump in service. On a scale of 1 to 10, a rating of 1 indicates a newly manufactured pump. Pumps demonstrating a maximum wear rating of up to and including a value of 3.5 at the end of the test, will be satisfactory in service, but where the overall pump rating lies in the range 4-6, service life will be reduced. A rating in this range therefore indicates a failure in the 1000 hour pump test. A rating in the

25

range 7-10 is linked to actual failure of the pump during the test. Where this occurs, the test is terminated before the completion of 1000 hours. As is well known to those skilled in the art, failures on extreme fuels can occur in less than 50 hours. The pump test method uses the Bosch VE distributor type injection pump; the 1000 hours test duration is based on field experiences.

30

It is surprisingly found that it is feasible to produce a diesel fuel composition containing ethanol which demonstrates a wear scar diameter (WSD) of less than 460 microns in the CEC F-06-A-96 HFRR test, but which in the separate CEC F-32-x-99 test involving a Bosch VE rotary distributor type diesel injector pump shows unacceptable wear patterns.

35

The reason for the apparent discrepancy between the normally adequate lubricity level of



460 microns WSD, and the unacceptable rotary distributor pump wear patterns which are observed with fuels containing ethanol, is believed to lie in the phenomenon of cavitation as hereinbefore described. Because of the propensity of fuels containing ethanol to cause cavitation within the body of a rotary distributor type diesel injection pump, it can be shown that a fuel meeting the criterion of acceptable lubricity in the CEC F-06-A-96 HFRR test (less than 460 micron WSD) fails to meet the criterion of acceptable life in the CEC F-32-x-99 pump rig test (i.e. the rating exceeds 3.5 after 1000 hours).

However, it is found that by addition of the following film-forming additives according to the present invention to a blend of diesel fuel and fuel alcohol, the problems of cavitation within the body of the pump are overcome, allowing a rating of 3.5 or less to be achieved after 1000 hours of operation. This may typically allow a satisfactory service life to be obtained with an otherwise unsatisfactory blend of diesel fuel and fuel alcohol.

#### Test results

##### Fuel blend sample number 2021943

A blend of fuel containing the following components was made up:

Swedish Class I diesel (sample number 2021940)	369.2 litres (92.3% vol/vol)
Ethanol	30.8 litres (7.7% vol/vol)
Cosolvent formulation	2kg

The cosolvent formulation is needed to produce a stable blend of ethanol in diesel fuel.

The co-solvent formulation used was AAE-05 available from O<sub>2</sub>Diesel Inc, Delaware, USA (previously AAE Technologies Inc.). It is understood to contain:

25wt% Surfactant A	C <sub>18</sub> diethanolamide
25wt% Surfactant B	C <sub>18</sub> fatty acid ethoxylated with average of 7 ethoxy groups
50wt% Co-solvent	50% C9 to C11 alcohol ethoxylate with average 2.5 EO groups per alcohol

##### Fuel blend sample number 2030834

A further blend of fuel containing the following components was made up:

Swedish Class I diesel fuel (sample number 2030831)	369.2 litres (92.3% vol/vol)
Ethanol	30.8 litres (7.7% vol/vol)
Cosolvent formulation	2kg

The co-solvent formulation was as above.

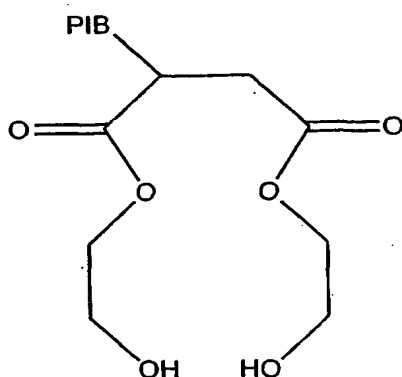
Fuel blend sample number 2030835

- 5 A further blend of fuel containing the following components was made up:

Swedish Class I diesel fuel (sample number 2030831)	369.2 litres (92.3% vol/vol)
Ethanol	30.8 litres (7.7% vol/vol)
Cosolvent formulation	2kg
Film forming additive	75mg/l

10

The co-solvent formulation was as above. The film forming additive used was:



wherein PIB was a polyisobutene having an average molecular weight of 260.

- 15 Lubricity tests were carried out using the HFRR apparatus according to the CEC-F-06-A-96 procedure, modified solely in respect of temperature of execution. (The standard procedure is executed at 60°C. Because of flash point concerns, the tests were carried out at 25 °C). The results of the tests are shown in Table 3.

20 Table 3 Test fuel HFRR data

Fuel tested	Sample number	Wear Scar Diameter, microns	
		Result at 60 °C	Result at 25 °C
Swedish Class I	2021940	606	624
Swedish Class I + Ethanol + cosolvent	2021943	-	324
Swedish Class I	2030831	614	646

Fuel tested	Sample number	Wear Scar Diameter, microns	
		Result at 60°C	Result at 25°C
Swedish Class I + Ethanol + cosolvent	2030834	-	342
Swedish Class I + Ethanol + cosolvent + film forming additive	2030835	-	321

These data show that the basefuel is not much affected by the alteration in test temperature. The data also show that the film forming additive does not contribute significantly to lubricity in these blends, since the results with and without the film forming additive are the same within test repeatability.

The fuel blends containing ethanol were also each subjected to a 1000h pump test using the Bosch VE rotary distributor pump according to the CEC F-32-X-99 method. The results of this test are given below:

10

Fuel blend containing no film forming additive : sample number 2021943 : Pump rating 4

Fuel blend containing film forming additive : sample number 2030835 : Pump rating 3

15 The fuel blend containing no film forming additive gives a failing or unacceptable result in the 1000h pump test. By contrast, the fuel blend containing the film forming additive gives a satisfactory, or pass result, in the 1000h pump test. Both fuel blends containing ethanol gave results in the HFRR test which would suggest a pass or satisfactory result in the 1000h pump test. However, only the ethanol fuel blend containing the film forming  
20 additive gave a satisfactory or pass result in the 1000h pump rig test. The difference in performance between the fuel blends is ascribed to inhibition or prevention by the film forming additive of the effects of cavitation within the pump, which would otherwise have increased wear rates as a result of the inclusion of ethanol in the fuel blend.

25 Details of the pump ratings are given in Tables 4 and 5 below

Table 4 Detailed pump rating : fuel sample 2021943

PRE TEST			POST TEST		
Ratings			Ratings		
Camplate:			Camplate:		
Path	n/a		Path	2.5	
Centre	n/a		Centre	2.5	
Claws	n/a		Claws	2.0	
Rollers	n/a		Rollers	3.0	
Roller bolts	n/a		Roller bolts	4.0	
Governor:			Governor:		
Flyweights	n/a		Flyweights	2.0	
Ring	n/a		Ring	2.0	
Supply Pump:			Supply Pump:		
Blades	n/a		Blades	2.0	
Raceway	n/a		Raceway	2.0	
Washer (plunger)	n/a		Washer (plunger)	2.0	
Overall rating	n/a		Overall rating	4.0	

5 Table 5 Detailed pump rating : fuel sample 2030835

PRE TEST			POST TEST		
Ratings			Ratings		
Camplate:			Camplate:		
Path	n/a		Path	2.5	
Centre	n/a		Centre	2.5	
Claws	n/a		Claws	2.5	
Rollers	n/a		Rollers	2.5	
Roller bolts	n/a		Roller bolts	3.0	
Governor:			Governor:		
Flyweights	n/a		Flyweights	2.0	
Ring	n/a		Ring	2.0	

PRE TEST		POST TEST	
Supply Pump:		Supply Pump:	
Blades	n/a	Blades	2.0
Raceway	n/a	Raceway	2.0
Washer (plunger)	n/a	Washer (plunger)	2.0
Overall rating	n/a	Overall rating	3.0

All publications mentioned in the above specification are herein incorporated by reference. Various modifications and variations of the described methods and system of the invention will be apparent to those skilled in the art without departing from the scope and spirit of the invention. Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes for carrying out the invention which are obvious to those skilled in chemistry or related fields are intended to be within the scope of the following claims.